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Applications and perspectives of phototrophic microorganisms for electricity generation from organic compounds in microbial fuel cells

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A B S T R A C T

There is an increasing interest to integrate phototrophic microorganisms into microbial fuel cells (MFCs) to assist electricity generation. In general, this integration can be accomplished in three ways: (1) phototrophic microorganisms function as or provide a substrate for supplying electrons; (2) photoheterotrophic microorganisms catalyze the anode reaction; and (3) photoautotrophic microorganisms provide oxygen as an electron acceptor to the cathode reaction. Direct use of phototrophic microorganisms for electricity production in MFCs faces significant challenges, because of the complex composition of microbial cells and their resistance to hydrolysis, and low conversion efficiency to electric energy by MFCs. Proper pretreatment using chemical or biological methods may improve degradability of microbial cells. Some purple nonsulfur bacteria exhibit strong electrochemical catalysis of organic compounds in the anode of an MFC, and the effect of illumination on the catalytic performance needs further investigation. Electricity generation via syntrophic relationship between photosynthetic microorganisms (providing organic compounds) and heterotrophic bacteria (oxidizing organics) in the anode is generally low due to low concentration of the electron donors and adverse effect of oxygen as a result photosynthesis on anode activities. It is promising to apply photosynthetic microorganisms in the cathode with multiple functions of oxygen supply, nutrient removal and biomass production. To address some of the challenges, two paradigms are proposed to encourage further investigation and development of effective processes with strong synergy between phototrophic microorganisms and MFCs.

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1. Introduction

Microbial fuel cells (MFCs) are an emerging technology that takes advantage of microbial interaction with solid electron acceptors/donors to convert organic compounds into electricity, which is then used to produce energy and other value-added compounds [1,2]. In the past decade, MFCs have been intensively studied from the aspects of configuration/operation, microbiology, electrochemistry, and application [3,4]. MFCs are modified to have additional functions such as hydrogen production and/or desalination, and the modified devices include microbial electrolysis cells (MECs) [5] and microbial desalination cells (MDCs) [6]. The potential applications of MFCs include wastewater treatment, remote power source for sensors, production of value-added compounds through electrochemical or electrosynthetic processes, and a research platform for understanding fundamental microbial respiration. One attractive feature of MFCs is direct conversion of the low-grade substrates such as wastewater into electricity, which is promising for sustainable water/wastewater treatment with a low carbon footprint. MFCs are capable of degrading various organic compounds including industrial and domestic wastewaters [7], its scale has been enlarged from milliliter to several hundred liters [8], and the long-term performance outside the laboratory has been examined [9]. However, the low efficiency (e.g., organics to electricity) is a great challenge for MFC development, and it is recognized that it will be beneficial to couple MFCs with other technologies to improve the efficiency, for example, MFCs can be integrated into a regular treatment process [10], and MDCs can be linked to either reverse osmosis or forward osmosis [11,12].

Among those integrations, phototrophic systems such as algal bioreactor is of particular interest for MFCs, because of the multiple benefits such as providing dissolved oxygen, nutrient removal, and biomass production [13]. Algal treatment of wastewater has a long history [14], especially in removing nutrients and heavy metals. The algal biomass produced from bioreactors can be used to produce biofuels such as biodiesel [15,16]. Producing algal biomass with wastewater provides an economically feasible biofuels option, benefiting from existing resources and infrastructure at wastewater treatment plants [17]. Algal bioreactors have been well studied for practical biomass harvest [18] and for removing nutrients from wastewater [19].

Integrating phototrophic microorganisms into MFCs occurred in the past 5–6 years with increasing interests in MFC technology [20,21], and there has been active research in microbiology and system development. Table 1 summarizes the major species (or mixed culture) of phototrophic microorganisms applied in MFCs. The objectives of this review are to provide an overview of current status of research in MFCs (including modified MFCs such as MDCs) containing phototrophic microorganisms and to analyze the challenges and perspectives of this biotechnology. It should be noted that the MFCs discussed here are different from some “photo-bioelectrochemical cells”, “photo-MFCs”, or similar processes in which the source of electrons is water [22]; in an MFC, electrons come from oxidation of organic compounds (including biomass of photosynthetic microorganisms). Thus, any work that performs water oxidation in the anode is excluded from this review, because they are different from typical “microbial fuel cells”, which requires the addition of organic compounds. In addition, this review does not include the photo MFCs based on plants.

2. Algal biomass as a substrate

Photosynthetic activities accumulate biomass, which can be used as an energy source via further conversion such as anaerobic digestion [23]. Likewise, algal biomass can also be used as a substrate for electricity generation in MFCs, either in living cells (cultivated or naturally occurred) or dry mass.

Table 1
Phototrophic microorganisms used in the MFC research.

Function	Species	MFC structure	References
Substrate	*Microcystis aeruginosa, Chlorella vulgaris*	Two chamber	[26]
Substrate	*Chlamydomonas reinhardtii*	Single chamber	[35]
Substrate	*Arthrospira maxima*	Two chamber	[34,44]
Substrate	*Chlorella vulgaris, Ulva lactuca*	Single chamber	[27]
Substrate	Scenedesmus	Two chamber	[28,71]
Substrate	*Laminaria saccharina*	Two chamber	[37]
Substrate	*Scenedesmus obliquus*	Two chamber	[30,32]
Substrate	*Chlorella vulgaris, Dunaliella tertiolecta*	Two chamber	[31]
Substrate	*Cyanobacteria*	Single chamber	[25,39]
Substrate	Mixed algae	Two chamber	[24,33,38]
Assisting Anode	*Chlorobium limicola*	Two chamber	[56]
Assisting Anode	*Rhodobacter sphaeroides*	Single chamber	[52]
Assisting Anode	*Rhodopseudomonas palustris*	Single chamber	[43]
Assisting Anode	*Rhodopseudomonas palustris*	Two chamber	[44]
Assisting Anode	*Chlamydomonas reinhardtii*	Single chamber	[55]
Assisting Anode	Mixed algae	Single chamber	[47,48,54]
Assisting Anode	Mixed culture	Two chamber	[46,49]
Assisting Cathode	*Chlorella vulgaris*	Two chamber	[58,61,64,65,69–71,73,74]
Assisting Cathode	*Chlorella vulgaris*	Three chamber	[63]
Assisting Cathode	*Chlorella vulgaris*	Single chamber	[72]
Assisting Cathode	*Desmodesmus sp.* A8	Two chamber	[60]
Assisting Cathode	*Microcystis aeruginosa* IPP	Two chamber	[68]
Assisting Cathode	Mixed culture	Two chamber	[57,59,62,66,78,79]

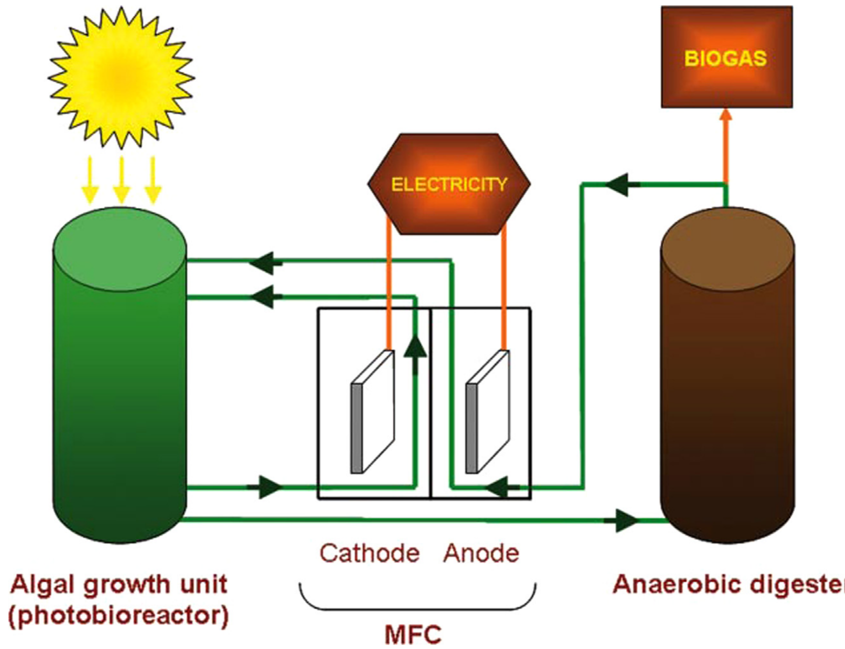

Fig. 1. A system for energy recovery from algae using anaerobic digester and an MFC. Reproduced with permission from Ref. [33].

2.1. Electricity generation from algal biomass

Living cells are usually obtained from cultivation in photobioreactors or natural sources. In an early effort, a photobioreactor that produced algal biomass was connected to an MFC, and provided living algal biomass as an anode substrate [24]. Electricity was successfully produced, demonstrating that algal biomass could be oxidized by bacteria in an MFC anode for producing electrons; however, the Coulombic efficiency of 2.8% indicated that the conversion efficiency of algal biomass into electricity was very low. Naturally accumulated algal biomass, for instance via eutrophication of natural water body that deteriorates water quality, can also be used for electricity generation in MFCs. A single-chamber MFC generated electricity from blue–green algae (cyanobacteria) and also effectively removed microcystins, which are the toxins that could harm aquatic life [25]. The treatment of algae in a two-chamber MFC lowered the chance of forming a disinfection by-product trihalomethane by removing its precursor [26].

Electricity generation was also achieved from dry mass in MFCs. In a single-chamber MFC, two types of dry mass were examined, and the biomass of microalgae *Chlorella vulgaris* resulted in higher energy recovery than that of macroalgae *Ulva lactuca* [27]. In another study, the dry mass of Scenedesmus was mixed with sludge as a substrate for an MFC; a higher amount of algal biomass resulted in a higher power density, but the authors did not analyze the contribution of electrons from sludge and algal biomass, respectively [28]. Algal powder was also used as an electron source to reduce chromium in a two-chamber MFC [29].

It is not expected that BES can completely degrade algal biomass, and thus metabolic products will be generated during electricity production. It was found that algal degradation in an MFC produced several byproducts, among which acetate and lactate were believed to be the major intermediate compounds responsible for electricity generation [30]. In a *C. vulgaris*-fed MFC, butanol was produced at 12.7–16.1 mM, much higher than 2.5–7 mM from *Dunaliella tertiolecta* [31]. By using analytic techniques such as UV adsorption and Fourier transform infrared (FTIR), the researchers revealed a sequential change of algal-derived organic matters during MFC degradation, following an order of protein-acidic functional groups-polysaccharides-amino acids [32].

2.2. Pretreatment of algal biomass

Because algal cell walls can be resistant to hydrolysis, pretreatment will be necessary to improve the conversion efficiency of algal biomass to electricity. Biological pretreatment is conducted by linking an anaerobic digester (AD) to an MFC; in that way, the AD acts as a pretreatment step for the MFC, or the MFC functions as post-treatment to polish the AD effluent. For example, a system consisting of a photobioreactor, an MFC and an AD was studied to have the algal cells treated in the AD for biogas production and then the AD effluent fed into the anode of the MFC for electricity generation (Fig. 1) [33]. In this system, the Coulombic efficiency reached 40%; however, because of a low COD (chemical oxygen demand) loading rate of 0.018 kg m^{-3} d^{-1} in the MFC, the maximum power production was only 0.25 W m^{-3}. In another study, cyanobacteria *Arthrospira maxima* was digested in an AD, and the AD effluent was further treated in a two-chamber MFC, which removed 67% of organic contents but had a low energy recovery ($<10.4\%$) due to a low Coulombic efficiency of 5.2% [34]. The function of the AD as pretreatment is to provide the easily-degraded organic compounds to electricigens through fermenting algal biomass. This role of fermenting bacteria was elucidated in an MFC with defined bacterial culture, in which the anode containing *Geobacter sulfurreducens* only did not generate any electricity from lysed cells of *Chlamydomonas reinhardtii* while adding an algal-digested bacterium *Lactobacillus amylovorus* into the *G. Sulfurreducens* solution significantly improved electricity output [35]. The MFC operation may also benefit AD for further removal of organic compounds and reduction of ammonia, a compound that could inhibit AD process, and this was demonstrated in an AD-MFC system using cyanobacterium *A. maxima* as the sole substrate [36].

Other pretreatment methods include heat, microwave, ultrasonic, acidic, alkaline, and extraction of algal organic matter (AOM). It was reported that either autoclave (for 15 min) or exposing algal cells to microwave irradiation (for 20 min) could improve electricity generation, compared with the untreated algal samples, likely because a higher COD concentration resulted from those two pretreatment methods [37]. Similar conclusion was reported in a study that used alkaline pretreatment that had algal

sludge for fermentation at constant pH 11 for 12 days and observed the improved power density and energy recovery in an MFC, compared with raw algal sludge; meanwhile, the COD degradation was more efficient with alkaline treated algal sludge [38]. Acidic fermentation of cyanobacteria increased the maximum power density by three times in a sediment MFC, even higher than the acetate-fed MFC [39]. Algal cells were also treated using combined acidic and autoclave methods [30]. Instead of using whole algal cells directly in MFCs, the researchers fed an MFC with the extracted AOM from two types of algae, *Microcystis aeruginosa* and *C. vulgaris*, and achieved more than 70% COD removal and energy recovery of 0.29–0.35 k Wh kg COD^{-1} [26].

3. Phototrophic microorganisms assisting the anode process

There have been quite a few studies of "photo MFCs" that contain photosynthetic microorganisms in the anode and can generate electrons through photo-catalytic reaction of water [40–42]. As mentioned earlier in the Introduction, those "photo-MFCs" are different from typical MFCs that produce electricity from organic oxidation, and thus are not included in this review. Involvement of phototrophic microorganisms in the anode of an MFC takes advantage of either their electrochemical-catalytic ability or production of organic compounds via photosynthesis that is then used for electricity generation.

3.1. Electrochemical-catalysis

The study of anode-respiring phototrophic microorganisms has been focused on photoheterotrophic bacteria, which can use organic carbon as a carbon source. A phototrophic purple nonsulfur bacterium, *Rhodopseudomonas palustris* DX-1, was isolated from the anode community of MFCs, and exhibited a very high activity in direct electron transfer to an anode electrode [43]. This strain could use a wide range of organic compounds, including acetate, lactate, fumarate, ethanol, and glycerol, which can be found in many domestic or industrial wastewaters. Further study found that *R. palustris* could also consume the whole cells of cyanobacterium *A. maxima* to generate electricity in two types of MFCs [44]. Because hydrogen is the product of organic oxidation by *R. palustris*, a hypothesis was proposed that suppressing hydrogen production might improve electricity generation by *R. palustris* in an MFC. This was examined by using gene manipulation to suppress hydrogen production, resulting in a higher power density by the mutant compared with the wild type [45]. *Rhodopseudomonas* was identified as a dominate cluster of bacteria with *Rhodobacter* in a phototrophic consortium on the anode of an MFC; this microbial community produced soluble electron mediators to assist electricity generation, and it was observed that illumination had a positive effect on electricity generation, but this phenomenon was not explained [46].

Identification of phototrophic bacteria and understanding their role in an anode community is important to future MFC application that involves mixed microbial community, instead of pure cultures. In a mixtrophic MFC system containing both anoxygenic and oxygenic phototrophs, electricity generation was higher under illumination than that in the dark despite higher dissolved oxygen with light, likely because anoxygenic phototrophs were dominant [47]. In a following study performed by the same researchers electricity generation from sewage was investigated using mixed microalgae as anode biocatalysts and found that dissolved oxygen was a major limiting factor on the MFC performance [48]. In those mixtrophic systems, electricity generation was low, and no information on Coulombic efficiency was reported; due to the possible presence of chemheterotrophic microorganisms in the inocula, the exact role of phototrophic microorganisms in electron transfer to the anode electrode remains unclear. By posing the anode potential unfavorably low for non-phototrophic electricigens and removing ammonia from the solution, phototrophic electricigens were enriched and produced electricity from acetate with a negative response to light [49]. Microbial analysis revealed green sulfur bacteria in the Chlorobia class were dominant phototrophs in the anode biofilm from both freshwater and salt water MFCs; non-phototrophic electricigens such as *Geobacter* were also detected [49]. Those results suggest that some phototrophic bacteria can play a key role in electricity generation in MFCs, and further studies of isolates from a functioning community are needed to understand their roles.

3.2. Substrate supply

Phototrophic activities can result in production of energy-rich compounds, such as hydrogen by photoheterotrophic bacteria or organic compounds by photoautotrophic microorganisms. Those compounds can be converted into electricity in an MFC through syntrophic relationship between phototrophic and electricigenic microorganisms. It should be noted that this approach is different from the supply of biomass of phototrophic microorganisms described in the Section 2.1: in the syntrophic activity, phototrophic microorganisms are alive and provide energy-rich compounds to electricigens via their phototrophic activities.

It is known that hydrogen produced by photoheterotrophic bacteria such as *Rhodobacter capsulatus* can be used as a substrate in a PEM fuel cell by linking with a photobioreactor [50]. This approach is simplified through integrating phototrophic bacteria into the anode of a fuel cell [51,52]. Moreover, the use of two-step biohydrogen production for electricity generation from organic compounds was accomplished through connecting dark fermentation (by *Escherichia coli*) and photo fermentation (by *Rhodobacter sphaeroides*) [53]. It was found that the rate of hydrogen oxidation was lower than hydrogen production, and the increased hydrogen pressure could inhibit further hydrogen production. In those systems, hydrogen oxidation is achieved with noble metal catalysts (e.g., platinum), which is different from typical MFCs that rely on microorganism to conduct electrons transfer to an anode electrode. The photoheterotrophic *R. sphaeroides* did not exhibit electrochemical-catalytic ability with organic compounds like that of *Rhodopseudomonas spp.,* as demonstrated by the insignificant electricity generation in the absence of platinum catalysts on the anode electrode (<0.01 mW m^{-2}) compared with that catalyzed by platinum (55–65 mW m^{-2}) [52].

Photoautotrophic microorganisms tend to produce organic compounds by using carbon dioxide as a carbon source. In a sediment-type MFC, it was believed that photosynthetic microorganisms (cyanobacteria) produced glucose that was then used by the anode microbes for electricity generation [54]. However, in such a mixed culture system with the presence of a large quantity of sediment, it was difficult to differentiate glucose produced photosynthetically and stored in the sediment, as the authors pointed out. Using defined binary cultures in an MFC, the researchers demonstrated that a non-phototrophic electricigen *G. sulfurreducens* could use formate produced by a green alga *C. reinhardtii* for generating electricity [55], which provides a proof of syntrophic relationship between two microorganisms during electricity generation. This relationship was further demonstrated in an MFC system containing either monoculture of isolated photosynthetic bacterium *Chlorobium*, electricigen *Geobacter*, or coculture of the two [56]. It was found that light-responsive current generation was observed only in the coculture MFC, which was likely from *Geobacter* oxidizing acetate produced from glycogen (via dark fermentation) that was released by *Chlorobium* during photosynthesis.

4. Phototrophic microorganisms assisting the cathode process

There has been a greater interest in applying phototrophic (mostly photoautotrophic) microorganisms in the cathode of an MFC with multiple benefits such as supplying oxygen, reducing carbon dioxide, producing valuable biomass, and/or polishing wastewater effluent.

4.1. Oxygen supply

Oxygen production as a result of photosynthesis is an attractive feature for the cathode process, because mechanic aeration consumes a large amount of energy. Almost all of the published work having photosynthetic microorganisms in the cathode takes advantage of this feature. Results from different researches demonstrate that current generation in an MFC can be stimulated by light illumination in the presence of photosynthetic microorganisms, and concurrent variation of dissolved oxygen provides strong evidences that the cathode reaction benefits from oxygen supplied via photosynthesis [57–61]. Affected by illumination condition/strength and reactor operation, the concentration of dissolved oxygen (DO) in a cathode compartment containing photosynthetic microorganisms varies from a few to above 20 mg L^{-1} [57,58,62], comparable to or better than mechanic aeration. Phototrophic biocathode was also studied in an MDC for driving desalination, and the results show that the MDC with microalgae *C. vulgaris* in the cathode removed 40.1% of salt, almost twice that of an abiotic cathode MDC [63].

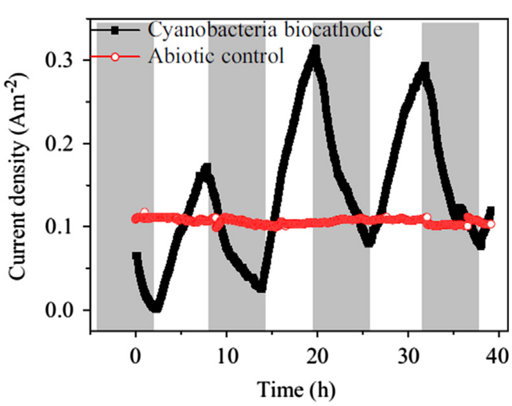

Fig. 2. Comparison of current generation between a cyanobacterial biocathode and an abiotic control. Reproduced with permission from Ref. [68].

The function of photosynthetic microorganisms for providing oxygen to a cathode electrode is clearly identified with pure culture studies (e.g., *C. vulgaris*), and the produced oxygen is reduced by accepting electrons from the cathode electrode [58,64]. It is also interesting to explore whether phototrophic microbes have more functions than "oxygen supply", for instance, being as a biocatalyst to catalyze oxygen reduction. An early study having *C. vulgaris* in the cathode concluded that *C. vulgaris* could act as an electron acceptor in the presence of an electron mediator [65]; however, lacking abiotic control experiment cannot exclude the possibility that oxygen was reduced by the cathode electrode, instead of *C. vulgaris*. Some studies detect electrochemical activities of the mixed-culture consortium [66,67]; because of the co-existence of non-phototrophic microbes possibly including electricigens, it is not distinguishable what role the phototrophic microbes are playing in electron transfer. A study of a cyanobacterium, *M. aeruginosa* IPP in the cathode, provided the first experimental proof that photosynthetic microorganisms can also catalyze the cathode reaction [68]. It was observed that the photosynthetic biocathode increased the current density by 245%, compared with the abiotic cathode that was aerated to maintain a certain level of DO (Fig. 2), and the reactive oxygen species (ROS) generated during photosynthesis such as hydrogen peroxide and superoxide anion radicals were found to be electron acceptors for electricity generation.

4.2. CO_2 capture

Carbon dioxide is a carbon source for photosynthetic microorganisms, and photosynthesis involves reduction of carbon dioxide. Thus, it is not unexpected that an MFC with a photosynthetic biocathode can "fix" carbon dioxide. Instead of externally supplying carbon dioxide, an interesting approach was developed to have photosynthetic microorganisms in the cathode of an MFC growing on carbon dioxide produced from its anode (oxidation of organic compounds) (Fig. 3), and such an MFC was named as "microbial carbon capture cell (MCC)" [69]. In this MCC, all the gaseous CO_2 generated from the anode was absorbed by the cathode used for growth of *C. vulgaris*, supported by the facts that no gaseous CO_2 was detected in the headspace of the cathode compartment and the level of inorganic carbon in the cathode remained unchanged

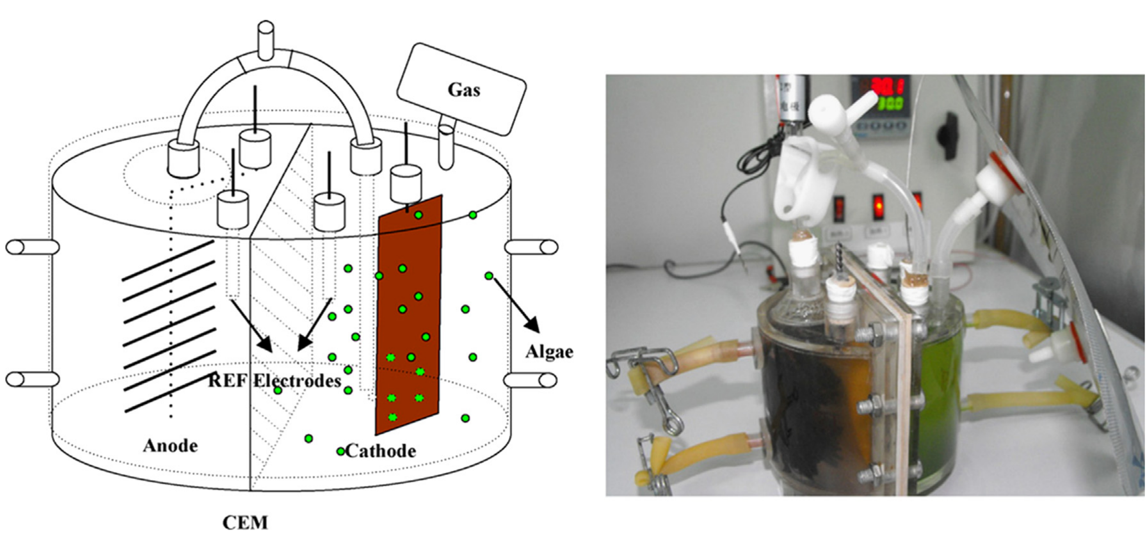

Fig. 3. A microbial carbon capture cell. Reproduced with permission from Ref. [69].

(while the control system in the absence of *C. vulgaris* had nearly six times increase in the concentration of inorganic carbon). A follow-up study of MCC by another group of researchers immobilized *C. vulgaris* by forming algal beads with sodium alginate and calcium chloride, and found that immobilization improved the maximum power density by 88% compared with the suspended algae [70]. The same immobilization procedure was examined in a study (though not in an MCC) with more detailed investigation of matrix concentrations, and the results demonstrated that optimization of a certain conditions such as cross-linking time and initial inocula concentration increased the power density by 258% [64]. Supply of CO_2 is largely affected by the anode activities and organic concentration in the anolyte. It was reported that at an initial anode organic concentration 2500 mg L^{-1}, the CO_2 production reached around 14%, which is within the range of optimal carbon level for the growth of *C. vulgaris* used in their MFC cathode [71]. The development of MCCs will help to make MFCs a carbon-neutral technology with strong sustainability.

4.3. Biomass production

As a result of photosynthesis, biomass of photosynthetic microorganisms is accumulated and may be used to produce energy or value-added compounds [15]. Biomass production was reported in several studies of MFCs with a photosynthetic cathode. Because of coexistence of both attached biofilm (on an electrode) and suspended biomass (in solution) in a cathode compartment, it is difficult to accurately quantify the total biomass, and the reported information mostly focuses on suspended biomass, except an early study found that biomass on the cathode electrode increased from 0.19 to 1.12 mg lipid phosphorus [66]. The concentration of biomass in the solution varies from 100 to more than 4000 mg L^{-1}. The highest algal concentration of 4060 mg L^{-1} was obtained in a sediment type single-chamber MFC; a high initial biomass concentration 3500 mg L^{-1} might contribute to the high value of biomass at the end of the experiment [72]. The highest biomass concentration in the two-chamber MFCs was 2800 mg L^{-1} [73]. It should be noted that biomass concentration can also be affected by hydraulic retention time (HRT). A long HRT (e.g., >10 days) tends to accumulate more biomass than a shorter HRT. For example, several fed-batch operated MFCs could produce >300 mg L^{-1} algal biomass at an HRT $>$ 10 days [59,63,71,74]; while a continuously operated integrated photo-bioelectrochemical (IPB) system with an HRT of 3 days (catholyte) produced a relatively low biomass concentration of 128 mg L^{-1} [57]. Algal biomass produced in an MFC can be used to extract pigment, which contains some high value compounds such as carotenoids, and composition of pigment was affected by light intensity and nutrient supply [73].

Conversion of the produced algal biomass to energy is of strong interest because it may offset energy supply or reduce energy consumption required by MFC treatment, and thus energy content of algal biomass is assessed. In the IPB system, the algal biomass represented an energy content of 0.057–0.085 kW h m^{-3}, significantly higher than the direct electric energy generated from the system, and with the energy from biomass the IPB treatment could theoretically be energy positive [57]. However, the authors admitted that the energy estimation from algal biomass did not include the energy consumption of treating algal cells. In a photo-MDC system, it was estimated that the produced algal biomass represented an energy content of 0.21 kW h m^{-3}, which further improved the energy benefits of this system to 2.01 kW h m^{-3} (without desalination energy credit); but the authors did not include the energy consumption by the MDC system (feeding and mixing that a large-scale system can hardly avoid) [63]. Nevertheless, harvesting energy from algal biomass produced in an MFC system is attractive, and proper assessment of energy benefit of this approach should consider multiple factors that consume energy involved in the system operation and algal conversion.

4.4. Wastewater treatment

The primary function of MFCs fed with wastewater is considered to be wastewater treatment, and thus the contaminant removal is a key parameter for evaluating MFC performance. In the most MFCs containing a photosynthetic cathode, wastewater (or synthetic organic solution to mimic wastewater) was only fed into the anode; although organic removal was achieved, the correlation between organic removal and cathode algal activities has not been well studied. In those systems, the cathode compartment would be filled with either buffer solution or defined medium for cultivating photosynthetic microorganisms, thereby creating a demand for additional water/nutrient supply. A large water footprint has been identified as a key challenge for commercializing algal bioreactors [75]. Alternatively, algal growth can be supported by wastewater, to achieve both contaminant removal and biomass production [76].

However, feeding raw wastewater into a cathode compartment will stimulate the growth of heterotrophic bacteria and organic compounds will act as an electron donor competing with the cathode electrode, which will damage the electricity-generating function of MFCs. A possible approach is to feed the wastewater treated by the anode into the cathode, and this treated wastewater will provide nutrients (e.g., nitrogen and phosphorus) for algal growth and may also be further polished by the cathode for removal of organic residues and nutrients. Very few studies have looked into this approach. An upflow type MFC had its anode effluent flowing through the cathode compartment, where algae were growing, and no information on contaminant removal by algae was reported [74]. A more detailed analysis was performed in an IPB system, in which the cathode compartment decreased the concentrations of nitrogen and phosphorus by 96% and 55%, respectively [57]. The organic concentration, on the other hand, was slightly reduced from 22 to 20 mg L^{-1} in the cathode of this IPB system. Those results demonstrate the feasibility of having a photosynthetic cathode fed with the treated anolyte and its effectiveness of nutrient removal, and encourage further development of photosynthetic MFC systems that can improve wastewater treatment while eliminate the requirement of additional water/nutrients.

4.5. Effects of illumination

Illumination is an important condition for growth of photosynthetic microorganisms, and the research mainly focuses on illumination intensity and length. Several studies found that increasing illumination intensity could significantly increase electricity generation, likely through improving the production of dissolved oxygen [60,64,73]. However, Juang et al. reported that their MFCs produced more electricity under lower light intensity [62]. Those results suggest that there are optimal light intensities for the MFCs with photosynthetic cathode, which will be related to microbial species and operating conditions. Adjusting light intensity can also affect the production of some valuable chemicals such as carotenoid in the cathode of an MFC [73]. A long illumination period may benefit oxygen production and thus electricity generation when illumination is a limiting factor. But an extended illumination was found to decrease electricity production, indicating that dark period is necessary to maintain a healthy community of photosynthetic microorganisms [57,58]. Increasing the frequency of light/dark cycle decreased the production of both electricity and algal biomass, confirming the importance of proper dark period for a photosynthetic MFC [57].

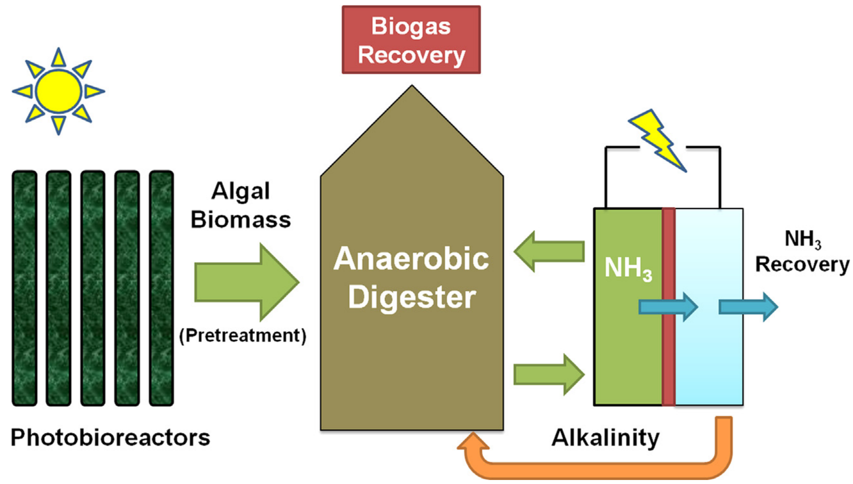

Fig. 4. A paradigm of an integrated system for energy production from algae consisting of a photobioreactor, an anaerobic digester, and an MFC.

5. Challenges and perspectives

5.1. Challenges

Despite great interests in applying phototrophic microorganisms for electricity generation in MFCs, we should also recognize the challenges associated with those applications, and proper understanding of the problems will help shape the direction of future research and development, which should consider the following issues:

- Direct use of phototrophic microorganisms as a substrate for electricity generation in MFCs may not be an optimal approach. The whole cells of microorganisms contain cell walls that are resistant to hydrolysis; even after a certain pretreatment, there are still complex compositions. MFCs do not have advantages in energy recovery from complex substrates compared with anaerobic digestion. For example, in an MFC system treating primary sludge, electric energy only contributed to 7–13% of the total energy production (while the rest was methane gas) [77]. Therefore, to utilize phototrophic microorganisms as a substrate for energy recovery, it will be more feasible to link MFCs to anaerobic digestion, as described by a proposed paradigm in the next section.
- It will be very challenging to have in situ use of photosynthetic products (e.g., organic compounds or hydrogen) for electricity generation in MFCs, because: (1) the amount of photosynthetic products is usually low (compared with biomass accumulation), and thus the energy potential for conversion will also be low; (2) oxygen is produced in some photosynthetic activities and will impair the anode activities; (3) allowing illumination to the anode compartment creates a significant challenge for reactor design and operation; and (4) when organic compounds are used as a substrate for photo-hydrogen production, competition between phototrophic and non-phototrophic microorganisms (in a mixed culture system) may severely affect phototrophic activities. Although not a promising method for large-scale energy production, this approach may be applied in sediment type MFCs for powering remote sensors.
- The role of illumination in electrochemical catalysis of the anode reaction by phototrophic microorganisms should be further investigated. Xing et al. found that illumination was not needed for current generation by a phototrophic purple nonsulfur bacterium *R. palustris* DX-1 [43]; while Cao et al. observed that illumination significantly improved electricity generation with a phototrophic consortium that contained the species in the clusters of *Rhodobacter* and *Rhodopseudomonas* [46]. The detection of soluble electron mediators in Cao's study may help interpret electron transfer mechanisms performed by the phototrophic consortium, and the relationship between the production of those electron mediators and phototrophic activities warrants further investigation.
- In some cases, one needs to choose between improving electricity generation and harvesting biomass. Immobilized algal beads were found to help improve oxygen supply and thus electricity production, but algal growth was slow in those beads. Therefore, we may not expect to harvest a significant amount of biomass by using algal beads. Non-immobilized algae (either attached in biofilm or suspended) will be more suitable for biomass production.
- Most studies focused on a pure strain of phototrophic microorganisms, while in a practical application (especially for wastewater treatment) mixed culture will exist in the bioreactor. More work will be needed to understand the activities of phototrophic microorganisms in a mixed microbial community and their interaction with other microorganisms (competition and/or syntrophic relationships). The stability of an MFC system containing phototrophic microorganisms should also be examined with actual wastewater and a long-term operation (several months to years; e.g., more than 12 months operation of the IPB system [57]).
- The design of MFC reactors must accommodate illumination (unless phototrophic activities are not required for MFC operation, such as the use of *R. palustris* DX-1 for catalyzing organic oxidation on the anode). The design could take advantage of the configuration of photobioreactors, and MFCs may be built in either tubular or flat configuration. The installment of electrodes and membranes will add on more difficulty when MFCs are scaled up. A paradigm example of an algal-MFC system is described in the following section.

5.2. Photo-MFC paradigms

To address some of the challenges described above, we propose the following system paradigms that link phototrophic microorganisms to MFC technology through either substrate supply (anode) or oxygen supply (cathode). The future research should not exclude other applications. We expect those paradigms will encourage more thinking and investigation of the synergy between phototrophic microorganisms and MFCs.

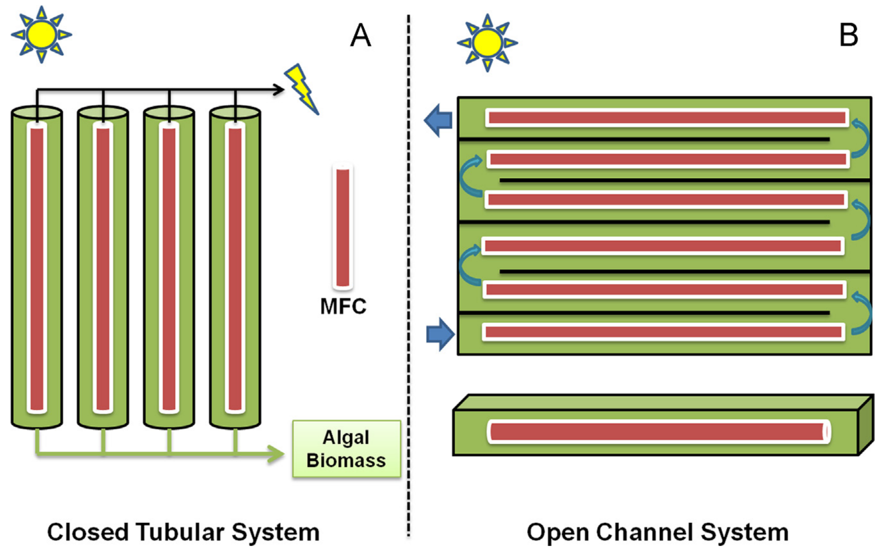

Fig. 5. A paradigm of algal bioreactor—MFC systems in either closed tubular (A) or open channel (B) configurations. The open channel system is shown in both top view and side view.

The first paradigm is a system designed for converting photoenergy into electric energy through degrading algal biomass (Fig. 4). This system consists of three units, photobioreactors, anaerobic digesters, and MFCs. The photobioreactors are to produce algal biomass though photosynthesis and biomass is supplied to the anaerobic digesters for biogas production. Pretreatment may be applied to improve the digestion of algal cells before the digesters. The digested liquid is recirculated through the anode compartment of an MFC for three purposes: (1) convert the products from digestion that cannot be further digested into electric energy; (2) reduce ammonia concentration to help stabilize the anaerobic digester [36] and possibly recover ammonia in the cathode; and (3) provide the alkalinity generated from oxygen reduction in the cathode to buffer the digestion liquid in the anaerobic digester. This system will produce bioenergy (biogas from anaerobic digesters that can be further converted into electricity and direct electricity production from MFCs), maximize organic conversion through two-step treatment, recover resources such as ammonia for fertilizer application, and reduce the cost associated with chemical addition (e.g., alkalinity) into the anaerobic digester.

The second paradigm focuses on cathode application of photosynthetic microorganisms for in situ oxygen supply and improved wastewater treatment (Fig. 5). The system can be designed as either closed tubular reactors (Fig. 5A) or open channel systems (Fig. 5B), which have MFCs installed inside algal bioreactors like what was described before [57]. Wastewater will be used as a single water stream fed into the MFCs first for organic degradation, and then the MFC effluent is discharged into algal bioreactors to support algal growth. Like the existing photobioreactors, the closed tubular systems may be more efficient but at a higher cost and with more construction/operating challenges. The open channel systems are relatively easy to construct and maintain, but algal production may be low. For small-scale application, the closed tubular systems may be appropriate, while the open channel systems are more suitable for large-scale operation (by taking advantage of the existing algal ponds).

6. Conclusions

The research has demonstrated the feasibility of incorporating phototrophic microorganisms in MFCs to assist electricity generation in several ways. Because of inherent problems of MFC technology such as low conversion efficiency, some integrations including direct use of algal cells as a substrate and using organics produced from photosynthesis in the anode may not be practical. Taking advantage of photo-oxygen production for cathode reactions with accumulation of valuable biomass could be more attractive, especially for wastewater treatment that can be accomplished by both MFC (organic removal) and photosynthetic microorganisms (nutrient removal), and provide water and nutrients for algal biomass at the same time. Future development of MFC system containing phototrophic microorganisms should consider synergistic cooperation with other processes such as anaerobic digestion to better use algal substrates, and integrate MFCs into the existing algal bioreactors (e.g., algal ponds).

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